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ELECTROLYTIC PREPARATION OF

HIGH DIELECTRIC THIN FILMS

by

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[7]

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Abstract

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This report covers the first quarter's work on a program to develop an electrolytic method for the preparation of high dielectric thin films. The method of preparation involves the anodization of a suitable metal substrate and inclusion of additives in the porous anodized film to produce an oxide composite analogous to high dielectrics prepared by ceramic techniques. A brief survey of recent literature on high dielectric materials has been carried out. Results of exploratory investigations on films prepared by anodization of Ti substrates are presented.

RUTHOR

Table of Contents

Abstract

I. Introduction

II. Literature Survey

III. Experimental

A. Approach

B. Film Formation on Ti Substrates

1. Cell Design
2. Ethyl Acid Phosphate Bath
3. Ethyl Acid Phosphate Bath Containing
Suspended Antimony Trioxide
4. Ethyl Acid Phosphate Bath Containing
Barium in Solution
5. Electrophoretic Depositions
6. Addition to Films by Dipping
7. Firing of Anodized Films

C. Evaluation of Anodized Ti Films by Capacity and Loss Measurements

1. Procedure
2. Results with Silver Paint Counter Electrodes
3. Results with Alternate Counter Electrodes

D. Discussion of Results

IV. Plans for Future Work

V. References

I - Introduction

The problem prompting this program concerns the need for microminiature capacitive elements in thin film form for use in integrated circuitry. Presently developed thin film capacitive elements are largely amorphous structures of relatively low dielectric constant and require large areas to obtain significant capacitance levels. The objective of this program is to develop procedures for the deposition of high dielectric materials on suitable ceramic - metal substrates in thin film form to provide structures suitable as capacitive elements.

The basic approach proposed for the preparation of these high capacity elements entails the formation of a porous oxide film coupled with the deposition of a second phase so as to produce a double-oxide composition. The porous oxide film is to be prepared electrolytically by anodization of a suitable metal substrate. The second phase is to be physically occluded in the porous film by the entrapment of ionic or finely particulate species during the anodization. Electrophoretic processes may be employed as an aid in achieving deposition of the second phase. An alternate approach would involve anodization of a suitable metal-alloy substrate to produce directly a composite oxide structure. The choice of metal substrate and addition agents -- and therefore of the final composite oxide -- will be governed by the presently available information on high dielectric compounds prepared by conventional ceramic techniques. Assuming dielectric constants of the order of 500 to 2,000, capacity values of 2 to 5 $\mu\text{F}/\text{cm}^2$ may be attainable for the thin films.

II - Literature Survey

The recent literature related to this project was approached through a search of Chemical Abstracts from January 1957 through June 1962. The search covered the oxygen-containing compounds of barium, calcium, cadmium, cobalt, copper, iron, magnesium, nickel, strontium, and zinc which also contain titanium, zirconium, niobium, or tantalum. The list of references so obtained was quite extensive. Since a complete treatment of the list is not needed and could not be justified, a representative cross-section of research in this period was made by using the years 1957, 1960, and Jan.-June 1962. The references for these years were considered in further detail, and the most promising (approximately 100) selected. In this survey it became apparent that one author (Smolenski) was outstanding. A complete survey was made on his work, and that of his principal co-worker (Isupov). The references are listed in Section V.

The principal distinctive peculiarity of ferroelectrics is the presence of a phase transition of the first or second order from a disordered state into a well ordered, polarized state (52).

As a result of this spontaneous polarization, the ferroelectrics possess more pronounced anomalies in the electrical and other properties than do most ionic crystals. At temperatures below the phase transition, the ferroelectrics show spontaneous deformations and a reduction of lattice symmetry (52).

The appearance of spontaneous polarization can be explained within the framework of the classical electrostatic interaction, since the internal field is determined by the reciprocal action of the dipoles which, in turn, are conditioned by a displacement of ions. An essential role is played not only by the long range (dipole) forces, but also by short range forces. Spontaneous polarization arises only when the elastic component of the restoration force occurring during a displacement of ions is less than the dipole forces (52).

Ferroelectrics and antiferroelectrics may be divided into two groups, depending upon whether or not they contain hydrogen. The first group (containing hydrogen) includes potassium sodium tartrate (Seignette salt, or Rochelle salt), phosphates and arsenates of potassium, and others. The second (not containing hydrogen) includes barium titanate, lead titanate, potassium niobate, and others. This second group is characterized by the fact that each cation is within an oxygen octahedron, and all or part of the cations have the electronic structure of a noble gas atom after giving up s and d electrons. The charge should be large and the ionic radius small (32).

In a typical ferroelectric substance of the oxy-octahedral type (such as BaTiO_3) there is a marked change in the dielectric constant with temperature, with an exceedingly high dielectric constant being observed within a narrow range. Each substance usually (but not always) has a single maximum lying between -200°C and $+400^\circ\text{C}$. The temperatures of these maxima and the breadth of the peak is commonly changed by the addition of a second substance. When a peak is broadened, it is usually lowered.

A number of compositions having high dielectric constants at room temperature have been selected from the literature and are presented in Table No. 1.

The reference most closely related to the present project is that of Maxwell (40). He formed a capacitor from titania containing 1% by weight antimony oxide. This small amount of antimony makes the TiO_2 conducting. This conductivity has been attributed to substitution of Sb^{3+} ions for some Ti^{4+} ions, resulting in Ti^{3+} ions and electrons free to move in the lattice as in n-type semiconductors. When electrodes are fired onto a conductive TiO_2 body, thin insulating layers on the surfaces of the body and a complete capacitor are produced simultaneously. The capacitor is of the layerized type. The equivalent circuit consists of two condensers in series with (and separated by) a resistance. Each of the condensers is also in parallel with a high resistance. This means that the effective capacitance occurs in thin layers at the two surfaces of the titania. This close spacing allows an increase in the effective dielectric constant from about 100 to 10,000 (for specimens 0.04 in. thick). It was found that these capacitors had a flat temperature characteristic.

III - Experimental

A. Approach

The general experimental approach to the preparation and evaluation

Table No. 1 Dielectric Constants of High Dielectric Ceramic Materials ($K > 500$)

Material (System)	Dielectric Properties at 25°C		Curve Having A Maximum Dielectric Constant		Upper Limit(°C)		Reference
	Frequency c/s	K	Temp. at Max., °C	K max	Lower Limit(°C) for K 500	for K 500	
BaTiO ₃	1 m	1113	120.	5100	-10.	170	40,45
Ba _{0.7} Sr _{0.3} TiO ₃	1 k	2000	70.	12,000	-100.	100	74
Ba _{0.7} Pb _{0.3} TiO ₃		5200	15.	6500			45
Bi _{0.5} K _{0.5} TiO ₃	500 k	600	390.	3400	25	450	96
CaTiO ₃	1 m	1677					40
CdTiO ₃	1 m	1600	60	1600	60	120.	76
(Ba,Pb)(TiSn)O ₃		5000					40
Semiconducting barrier layer titanates, such as (Ba,Sr)TiO ₃ -x							
BaTiO _{0.85} Sr _{0.15} O ₃	500 k	500,000	20	14,000	-70	150	40
BaTiO _{0.85} Zr _{0.15} O ₃	500 k	11,500	65	9000	-5	100	45
(Ba,Pb)ZrO ₃		1000					40
Na Nb O ₃		6000					40
K Nb O ₃		500					40
BaO _{0.4} Pb _{0.6} Nb ₂ O ₆	1 k	700					80
BaO _{0.25} Sr _{0.25} Pb _{0.5} Nb ₂ O ₆	1 k	1100	300	5500	0	400	
Pb _{0.5} Fe Nb O ₆	300 k						
Pb _{0.5} MgNb _{0.5} O ₆	1 k	1300	120	6500	-50	400	80
(Na,Cd)NbO ₃	1 m	8000	110	5500	-100	250	93
NaNbO ₃ -Sr ₂ Ta ₂ O ₇	1 k	1000	-10	13,000	-150	100	86
		2600					40

of potential high dielectric thin films has been outlined in a previous document¹⁰⁵. Composite oxide films from the system of titanates, niobates, zirconates and tantalates have been chosen for investigation¹⁰⁶. Special emphasis will be placed on the titanates.

The selection of an anodizing bath for Ti and an examination of the film formation parameter was chosen for immediate attention. The effect of second component additives to the bath with respect to film formation and compatibility with the electrolyte could be examined at an early stage. Because of the relatively well known high dielectric qualities of the family of alkaline earth titanate ceramics, the development of methods for the incorporation of alkaline earth oxides into the anodized film was given a high priority.

It is to be expected that the composite films will require a heat treatment or sintering step to achieve maximum properties. The films will be treated in various available furnaces to indicate the limits of time, temperature, and environment that the anodized structures can withstand.

Initial evaluation of apparently mechanically sound films will be in terms of capacity and electrical loss values as measured by the use of counter electrodes on the film surface. Different types of counter electrodes (liquid, solid) and their methods of application (painting, vacuum deposition, etc.) will give different levels of response on a given surface. The responses of a selected list of counter electrodes on the types of film surfaces produced should be evaluated at an early date.

The results of Sibert¹⁰⁷ on the anodization of Ti surfaces indicate that acid phosphate based baths, and in particular aqueous solutions of ethyl acid phosphate, possess superior anodic film forming characteristics. Maxwell¹⁴⁰ has found that an effective high dielectric ceramic can be produced by small additions of Sb_2O_3 to fired TiO_2 . The anodization of Ti in an ethyl acid phosphate bath with and without Sb_2O_3 appeared to be a logical point for initiation of the study.

B. Film Formation on Ti Substrates

1. Cell Design

For these initial experiments a simple cell design was chosen. The anodizing bath was contained in a 250 ml Griffin beaker filled to near the top. A cylinder of Ti metal foil three inches high and $2\frac{1}{2}$ inches in diameter served as the cathode. The Ti metal to be anodized was cut from 5 mil sheet (Titanium Co. of America, No. 55A) into strips three inches long and from $5/16$ to $\frac{1}{2}$ inch wide. A stop-off jig and anode support was provided by sandwiching $1\text{-}3/4$ inches of the strip length between two sheets of silicone rubber backed by stiff plastic and held tight with a c-clamp. The jig was immersed approximately $\frac{1}{4}$ inch into the surface of the bath with the longer section of exposed Ti strip extending one inch down the axis of the cell. The short length of the strip extending above the jig served as the anodic connection to the power supply. The bath was stirred with a magnetic stirring bar. Power was supplied to the cell by DC voltage supplies which could be both current and voltage regulated.

2. Ethyl Acid Phosphate Bath

Typical film formation times are given in Table No. 2 as a function of the pre-set voltage limit and current density. The baths were 25 volume percent aqueous solutions of ethyl acid phosphate (Virginia-Carolina Chemical Corp.) which will be abbreviated to $E+H_2PO_4$. For strips numbered 7 or 11 a suspension of Sb_2O_3 was also present in the bath.

Upon the application of power the current rose immediately to the preset level while the voltage rose slowly. When the voltage reached the pre-set value the current dropped abruptly to less than one ma. At this point the strip was removed from the bath, rinsed with distilled water and dried at $110^\circ C$.

The films prepared under the conditions listed were a uniform light gray with a rough surface texture observable at 45X magnification. No holes or cracks could be observed up to 90X.

Table No. 2

Anodizing Ti Strips at 100 ma. in the $E+H_2PO_4$ Bath

<u>Strip No.</u>	<u>Pre-Set Voltage</u>	<u>Time to Limit (Seconds)</u>	<u>Current Density (ma/cm²)</u>
29A	190	85	16
2	195	70	28
29C	195	80	16
11D	200	90	14
33C	215	165	14
7A	220	125	29
29B	220	190	16
33A	220	210	13
11B	330	600	19
14E	360	900	16
14F	370	1260	15

In the neighborhood of 360 to 370 volts the film breaks down in the area just under the jig where large gas bubbles collect. (Increased gas formation on the anode is observed as the voltage rises). After breakdown the current continues to pass at the pre-set level. Debris is formed on the arced areas. On the balance of the strip a new type of film begins to grow. At 100 ma the base film is covered with white dots. After a few minutes at 600 ma the entire surface is covered (except for a few pinholes) with a thick, white, glazed-appearing layer.

Unless otherwise indicated, the Ti strips were anodized without prior treatment. When a dilute HNO_3 -HF pickle was used, the typical, relatively thick gray films could not be prepared. Instead, thin, translucent, colored and unevenly thick films were obtained.

3. Ethyl Acid Phosphate Bath Containing Suspended Antimony Trioxide

Two gm of reagent grade Sb_2O_3 was added to a 250 ml $\text{E}+\text{H}_2\text{PO}_4$ bath and dispersed by stirring. After several hours a suspension of fine particles was obtained. Titanium strips were anodized in this bath shortly after the addition and again when the suspension had been obtained. The resultant films appeared identical to those prepared in plain $\text{E}+\text{H}_2\text{PO}_4$ baths.

4. Ethyl Acid Phosphate Bath Containing Barium in Solution

Twenty gm of reagent grade $\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ in 100 ml water was dissolved using the minimum quantity of concentrated H_3PO_4 . Additional H_3PO_4 was added (a few ml) to PH 0.8. Sixty five ml of $\text{E}+\text{H}_2\text{PO}_4$ was added and the solution diluted to 250 ml.

The anodized Ti films prepared in this bath exhibited a breakdown potential of 115 volts. Below this potential only, thin, translucent, gold-purple film were formed. When a Ti strip anode was employed, which had been pre-anodized in a plain $\text{E}+\text{H}_2\text{PO}_4$ bath, no current passed below 115 volts. At higher applied potentials the surface of the film was pitted by sparks.

Films for evaluation were prepared at 110 volts. Some were then over-coated with films prepared in a plain $\text{E}+\text{H}_2\text{PO}_4$ bath.

5. Electrophoretic Depositions

Reagent grade CaO slurried in isopropanol gave an electrophoretic deposit on Ti strips, pre-etched in HNO_3 - HF , when the strips were made 260 to 400 volts negative. The same cell geometry as used for the anodizations was employed. No attempt was made at this time to classify the particle size. The deposits were thick and non-uniform, and coverage was not complete. The deposits adhered to the strips on heating to 800°C and rapid cooling.

The CaO deposit dissolved rapidly in the strongly acid $\text{E}+\text{H}_2\text{PO}_4$ bath even after heat treating. Anodized films on the previously CaO -coated strips exhibited darker and lighter areas. The latter were caused by particles (presumably CaO) imbedded in the film.

A suspension of BaTiO_3 particles in pyridine produced very thick (the order of mils) electrophoretic deposits on Ti strips held 250 volts negative. Excellent coverage was obtained in 25 seconds. The BaTiO_3 deposit did not appear to dissolve in the $\text{E}+\text{H}_2\text{PO}_4$ bath, but a good deal of it was dislodged on anodization. Films, anodized over the BaTiO_3 deposit, contained particles of imbedded BaTiO_3 .

6. Additions to Films by Dipping

Strips of Ti having freshly dried anodized films were dipped into a solution of barium acetate and dried. The procedure was repeated until the weight gain of the strip indicated that sufficient barium values had been added to very roughly approximate the number of mols of Ti present in the film. The weight gain was not adequate until a thick deposit was layed down on the surface of the film.

7. Firing of Anodized Films

Anodized strips of Ti were heated to 1100°C for 30 minutes in a graphite lined induction furnace in an atmosphere of argon. The exposed Ti metal was severely corroded and the films were destroyed. At higher temperatures the effects were accelerated.

The anodized strips were routinely fired in air for one hour at 800°C and cooled rapidly. No cracking or peeling of the films was observed. The films formed under the conditions listed in Table No. 1 turned dark gray on firing. The very thick films, prepared at high voltage and high current, remained white. No defects -- holes or cracks, could be observed in the dark, fired films at 90X magnification. Except for the color change, all the 800°C fired films appeared identical to unfired films.

Firing of HNO₃ - HF etched Ti at 800°C produced a dark blue film (as opposed to the normal gray film obtained on untreated Ti). The blue Ti could then be anodized to produce a normal film in the same manner as unetched Ti.

C. Evaluation of Anodized Ti Films by Capacity and Loss Measurements

1. Procedure

Counter electrodes were applied to the anodized Ti strips prepared as described in Section III B. For the most part, silver paint counter electrodes were employed. One or more areas on each film were painted with Wornow Process Co., silver ink no. 140-15-U to give electrode areas of 0.3 to 0.8 cm². The painted strips were then baked at 110°C to cure the paint. Aqueous electrodes were obtained by defining an area with electrical tape and adding a drop of concentrated LiCl soln. The mercury electrodes were contained in a ground-end glass tube pressed firmly against the film surface. Chromium metal counter electrodes were prepared by vacuum deposition. The unanodized section of the Ti strip served as the other electrode.

Capacity and loss values were obtained for the areas of the anodized films under the counter electrodes by measurement on a General Radio, Model 1650-A, capacity bridge at 1000 cycles/sec with signal strengths of the order of 10 millivolts. The loss is given by the "D" value. When D is less than unity in the following tables, the series equivalent circuit is implied; and when greater than unity, the parallel equivalent circuit.

2. Results with Silver Paint Counter Electrodes

Table No. 3 lists the results of measurements made on films with various concentrations of Sb₂O₃ slurry in the E+H₂PO₄ anodizing bath. Among the parameters that were varied, Sb₂O₃ concentration, anodizing voltage, current density, and silver paint baking time, only the baking time appears to seriously affect the capacitance and loss values obtained. For films fired at 800°C the presence of Sb₂O₃ in the anodizing bath does not appear to have enhanced the capacity. The C and D values obtained may be considered as typical values for one component films fired at 800°C.

Table No. 3

Capacity and Loss Values Measured With Silver
Paint Electrodes on Ti Strips Anodized in an
 $E+H_2PO_4$ Bath and Fired at $300^\circ C$

Strip No.	Sb_2O_3 Slurry Conc.	Ag Paint Baking Time (hours)	Maximum Voltage	Current Density (ma/cm^2)	Capacity (nF/cm^2)	Loss (D)
7A	None	1	220	29	4.9	0.035
7C	Thin	1	220	29	4.2	0.028
7F	Thin	$\frac{1}{2}$	220	29	4.9	0.043
7H	Heavy	$\frac{1}{2}$	220	29	4.1	0.043
7J	Heavy	$\frac{1}{2}$	220	29	3.9	0.044
77A	None	17	220	29	5.8	0.045
7C	Thin	17	220	29	4.9	0.048
**						
7F	Thin	250	220	29	7.2	0.029
7H	Heavy	250	220	29	6.8	0.040
7J	Heavy	250	220	29	6.7	0.032
11D	Heavy	15	200	14	5.5	0.050
11C	Heavy	15	250	17	4.3	0.055
11A	Heavy	15	280	17	4.3	0.050
11B	Heavy	15	330	19	5.0	0.050

Very limited measurements on non-fired, untreated $E+H_2PO_4$ bath films, using silver paint counter electrodes, indicate that a slightly lower capacity is obtained than for the $300^\circ C$ fired films.

Films anodized over Ti strips containing electrophoretic CaO deposits gave the same range of values as those listed in Table No. 3.

Table No. 4

Capacity and Loss Values Measured with Silver Paint Electrodes
(Baked 60 Hours) on Ti Strips, Parts of which were Covered
With Electroporetically Deposited $BaTiO_3$, Anodized at 250 Volts
in the $E+H_2PO_4$ Bath, and Fired at $300^\circ C$

Strip No.	Measured Over $BaTiO_3$ Precoat Area	Current Density (ma/cm^2)	Capacity (nF/cm^2)	Loss (D)
26Aa	No	18	6.7	0.033
26Ab	No	18	6.0	0.035
26Ac	Yes	18	7.3	0.030
26Ad	Yes	18	6.8	0.031

Table No. 6

Average Capacity and Loss Values Measured With
Vacuum Deposited Chromium and Mercury Electrodes
on Ti Strips Anodized at 14 ma/cm² to 215 Volts in an E+H₂PO₄ Bath

Strip No.	Electrode Type	Fired to 800°C	Average Capacity (nF/cm ²)	Average Loss (D)
33D34	Cr	No	17	0.043
33A34	Cr	Yes	1000	0.50
33F40	Hg	No	2.4	0.025
33B40	Hg	Yes	1.4	0.050

D. Discussion of Results

The capacity values measured on the 800°C --- fired films prepared in the E+H₂PO₄ bath on Ti Strips are essentially the same as those reported in the literature¹⁰⁷ for non-fired films using silver paint counter electrodes (reported values of 5.5 to 7.5 mF/cm² at D = 0.01 to 0.026). The "D" values from this work tend to be slightly higher, but this is to be expected on the basis of a higher porosity. The films pores were not "healed" in the bath by anodizing for extended periods at the reduced current. In addition, the firing has probably caused the formation of additional microcracks and holes.

The results of these exploratory anodizations with Sb₂O₃ particles in the bath or anodizations over electrophoretically deposited CaO or BaTiO₃ particles are, of course, indeterminant. The size of the unclassified particles was probably much too large and the firing temperature of 800°C much too low to effect an interaction (high dielectric ceramics are usually prepared at 1300 to 1400°C). It is encouraging to note that the presence of particles does not affect the film formation. The ability to grow thick films quickly at high current densities might be especially useful for the incorporation of particles within the film.

The presence of large amounts of dissolved barium in the E+H₂PO₄ bath appears detrimental to the preparation of useful films under ordinary conditions of film formation. This problem might be overcome by the use of high current densities if the sparking can be limited to a small area.

The films dried at 110°C do not appear sufficiently porous to allow the incorporation of significant quantities of liquid by dipping. Increased amounts might be added by dipping under vacuum, especially if the films were rendered more porous by firing or high current preparation.

Table No. 4 (continued)

26Ba	No	3	5.7	0.033
26Bb	Yes	3	5.7	0.033
26Bc	Yes	3	6.0	0.032

When the thin, colored films prepared from the $E+H_2PO_4$ containing barium phosphate in solution were fired at $300^\circ C$ and supplied with silver paint counterelectrodes, slightly higher capacities and much higher D values were obtained than for simple $E+H_2PO_4$ bath films. When these thin films were overcoated with films from the $E+H_2PO_4$ bath, typical, $E+H_2PO_4$ bath C and D values were obtained.

3. Results with Alternate Counter Electrodes

Table No. 5

Capacity and Loss Values Measured with Aqueous LiCl
Electrodes on Ti Strips Anodized at 16 ma/cm^2 in an $E+H_2PO_4$ Bath

Strip No.	Maximum Voltage	Fired at $300^\circ C$	Capacity (nF/cm^2)	Loss (D)
29Ba	220	No	33	0.12
29Bb	220	No	39	0.11
29Da	220	No	33	0.036
29Db	220	No	35	0.064
29Aa	190*	Yes	1900	0.6
29Ab	190*	Yes	5000	1.0
29Ca	195	Yes	1200	0.5
29Cb	195	Yes	1400	0.8

* Film kept at voltage for 15 minutes after current dropped to a low value.

The C and D values measured with the aqueous LiCl counter electrode bath increase with time. The values listed in Table No. 5 are for 10 to 15 minutes after application of the liquid.

Firing for one hour to 300°C does not appear to be detrimental to the gross mechanical strength or adhesion to the substrate of the anodized Ti films. Improved firing procedures will have to be developed to achieve long heats at significantly higher temperatures.

The very high capacities observed for 300°C fired films with aqueous or vacuum deposited Cr counter electrodes may be due to the creation of a semiconducting, barrier type dielectric⁻⁴⁰ or simply due to the formation of deep pores or cracks in the films. In the latter case the liquid or metal atoms may have penetrated deeply into the film to give an extremely small effective thickness. With the use of non-penetrating silver paint or mercury counter electrodes, the high capacity is not observed.

The relatively non-porous, non-fired films exhibit better than a two-fold increase in capacity (at the same loss value) when measured with the vacuum deposited Cr counter electrodes as compared to the baked silver paint electrodes. This improvement is probably due to a better conformation of the vacuum deposited layer with the rough surface of the anodized film thereby giving an increased effective area of contact per apparent unit area of film.

IV Plans for Future Work

Short firing periods at high temperatures will be tried on anodized Ti strips by direct inductive coupling to the Ti substrate. Any higher temperatures achieved should tend to increase the interaction of the materials present in the mixed component films.

High current density anodizations on Ti will be carried out to determine whether more particles or ions can be trapped in the more quickly formed, thicker films. This can be done in conjunction with the use of sub-micron size particles that more closely approach the thickness of the film produced.

The inclusion in the film of particles which are high dielectrics in themselves (such as BaTiO_3) appears promising. Such composite films could yield a high average dielectric value without the necessity of firing at elevated temperatures.

Particles can be first layed down on a Ti metal substrate. The deposit could then be filled and covered with Ti metal by vacuum deposition or electrodeless deposition from a fused salt. Anodization of the resultant composite could lead to a better chance of entrapment of particles within the film and better protection of soluble particles from dissolution by the anodizing bath.

Filling a more porous film with liquid under vacuum can be attempted. Several applications of the liquid with drying or firing steps in between could conceivably put a significant amount of additive into the film. The addition of significant amounts of a low-level doping type additive could probably be achieved in one step, possibly even without the vacuum.

The experiments outlined above are an outgrowth of the exploratory work performed on Ti substrates. Whole new areas of the project remain to be explored, principally the use of alternate substrate (Nb, Zr, Ta) and alloy substrates.

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